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# RHEOLOGICAL BEHAVIOUR OF THERMOPLASTIC POLY(ESTER-SILOXANE)S

*Two series of thermoplastic elastomers (TPES), based on poly(dimethylsiloxane) (PDMS) as the soft segment and poly(butylene terephthalate) (PBT) as the hard segment, were analyzed by dynamic mechanical spectroscopy. In the first TPES series the lengths of both hard and soft segments were varied while the mass ratio of the hard to soft segments was nearly constant (about 60 mass%). In the second series, the mass ratio of hard and soft segments was varied in the range from 60/40 to 40/60, with a constant length of soft PDMS segments. The influence of the structure and composition of TPESs on the rheological properties, such as complex dynamic viscosity, $\eta^*$, the storage, G', and loss, G", shear modulus as well as the microphase separation transition temperature, $T_{MST}$, was examined. The obtained results showed that the storage modulus of the TPESs increased in a rubbery plateau region with increase in degree of crystallinity. The rheological measurements of TPESs also showed that a microphase reorganization occurred during the melting process. The microphase separation transition temperatures were in the range from 220 to 234 °C. In the isotropic molten state, the complex dynamic viscosity increased with increasing both the content and lenght of hard PBT segments.*

Thermoplastic elastomers possess an extraordinary combination of physical properties, such as elasticity, low-temperature flexibility, impact strength, toughness and easiness of processing (extrusion, injection molding, etc.) [1,2].

Poly(organosiloxane)-containing block copolymers, which belong to the class of thermoplastic elastomers, have been extensively studied and described frequently in the literature [3–21]. PDMS-containing block copolymers show a phase-separated microstructure. Microdomains rich in hard-segments, resulting from intermolecular actions such as crystallization or hydrogen bonding, form so-called physical crosslinks and guarantee good mechanical strength, while the soft, amorphous PDMS matrix improves flexibility. The incorporation of PDMS-segments into a PBT-backbone results in improved clarity, surface smoothness and non-sticking properties, as well as good film, fiber and hydrophobic properties of the resulting copolymers [21–27]. Poly(dimethylsiloxane) and its block copolymers have many interesting and desirable properties, such as a very low glass transition temperature (–123 °C), excellent thermal stability in both inert and oxidizing environments, resistance to UV radiation, ozone and atomic oxygen, low surface tension, low surface energy, physiological inertness and high gas permeability [3,28]. Combination of the properties of PBT and PDMS makes the resulting block copolymers excellent candidates for surface modifying additives, drug encapsulation and biomaterial applications [29,30].

In our previous papers [11–14], the synthesis, structure and properties of different thermoplastic poly-(ester-siloxane)s, based on PBT as the hard segment and PDMS as the soft segment were described. The obtained TPESs differed in the functionality of the end-terminated poly(dimethylsiloxane)s (i.e. either silanol- or carboxypropyl-) which were incorporated into the polyester-backbone as flexible segments.

Dynamic mechanical measurements can provide a good insight in the phase behavior of thermoplastic poly(ester-ether) [31–33], poly(ester-ether-siloxane) [4,10,15] and poly(ester-siloxane) [14,16] elastomers based on hard PBT segments. In the molten state, these systems typically form a homogeneous mixed phase of soft and hard polyester segments. Upon cooling, at a certain temperature the polyester segments start to crystallize. There is evidence that crystallization starts from a homogeneous melt and that the crystallization process is the driving force for phase separation. Upon further cooling to room temperature, a phase-separated structure, consisting of PBT crystallites embedded in an amorphous matrix is obtained. The lamellar hard domains in thermoplastic polyester elastomers are very regular in size and shape, similar to the structure observed for PBT homopolymers. Under certain crystallization conditions, the lamellae of the hard segments organize into a spherulitic structure, which is the characteristic structure of the common semi-crystalline polymers [1,2,33].

In the present work two series of thermoplastic poly(ester-siloxane)s based on carboxypropyl-terminated PDMS prepolymer [12,13] were analyzed by dynamic mechanical spectroscopy. In the first poly(ester-siloxane) series the mass ratio of hard to soft segments was nearly constant (about 60/40), while the lengths of both the hard and soft segments were varied [12]. In the second TPES series, the mass ratio of hard to soft segments was varied from 60/40 to 40/60, while the length of soft PDMS segments was kept constant [13]. The influence of the structure and composition on the complex

dynamic viscosity, $\eta^*$, the storage, $G'$, and loss, $G''$, shear modulus and the microphase separation transition temperature, $T_{MST}$, was examined by dynamic mechanical spectroscopy.

Finally, it can be mentioned that by changing the copolymer composition, the mechanical characteristics of the TPESs can be tailored and adjusted to the different purposes, such as surface modification and medical applications (for example, films and microspheres for controlled drug release).

## EXPERIMENTAL

### Samples

Two series of thermoplastic poly(ester-siloxane)s were synthesized by two-phase catalyzed transesterification reaction in the melt. Details of the copolymer synthesis and characterization have been reported elsewhere [12,13].

### Measurements

The TPES rectangular bars and discs for the dynamic mechanical analysis were prepared by press molding from melt at 250 °C and 3 MPa, and cooled rapidly.

Dynamic mechanical analysis was performed using a Rheometrics mechanical spectrometer RMS-605, under torsion rectangular conditions on molded polymer bars (63.0 mm×12.4 mm×1.0 mm), in the temperature range from 30 to about 200 °C (when the samples have been ruptured). The rheological measurements of the TPESs melts ($\eta^*$, $G'$ and $G''$), were performed in the dynamic shear mode between two parallel plates in the tempe-

rature range from 170 to 250 °C. The frequency was varied from 0.1 to 100 rad/s. The radius of the samples was 25 mm while the thickness was about 1.0 mm.

## RESULTS AND DISCUSSION

The molecular structure of the investigated TPESs based on the carboxypropyl terminated poly(dimethylsiloxane) prepolymers, is presented in Figure 1. Two series of TPESs were prepared by catalyzed two-step, melt transesterification reactions of dimethyl terephthalate and methyl-esters of carboxypropyl terminated poly(dimethylsiloxane)s with 1,4-butanediol [12,13].

In Series I, molar masses, $\overline{M}_n$, of carboxypropyl terminated poly(dimethylsiloxane) prepolymers determined from $^1$H-NMR spectra were 550, 870, 1190 and 2170 g/mol, while the mass fraction of the hard segments was about 60%. In this manner four TPES samples (TPES 1-4) with different hard and soft segment lengths were obtained (Figure 2a) [12]. The average degree of polymerization of the hard PBT segment ($\overline{X}_n$) increased simultaneously from 3.8 to 16.9 with increasing molar mass of the PDMS prepolymer (Table 1).

The composition of the starting reaction mixtures in Series II was selected to result in copolymers with a hard to soft segment mass ratio of 70/30, 60/40, 55/45, 50/50 and 40/60, while the molar mass of the PDMS prepolymer was constant ($\overline{M}_n$ = 1030 g/mol). In this manner, five TPES samples (TPES 30-60) with constant soft, but different hard segment lengths, were obtained (Figure 2b) [13]. The average degree of polymerization of the hard PBT segments, $\overline{X}_n$, increased simultaneously from 3.1 to 15.4 with increasing the mass ratio of hard to soft segments (Table 1).
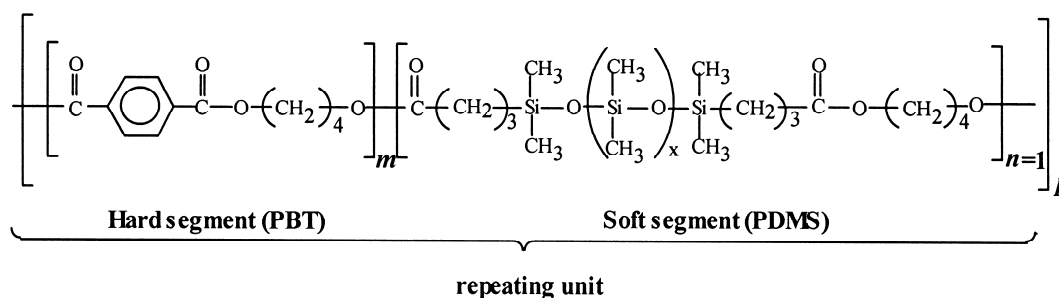


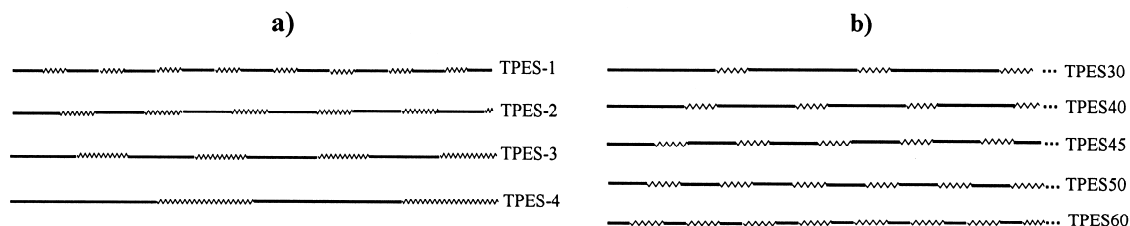*Figure 1. Chemical structure of the TPES.*



*Figure 2. Schematic representation of TPESs with: a) different lengths of the hard (—) and the soft (⌇⌇) segments (Series I) and b) constant length of the soft (⌇⌇) segments but different lengths of the hard (—) segments (Series II).*

*Table 1. Molar masses of PDMS segments and TPES copolymers, $\overline{M}_n^{PDMS}$, $\overline{M}_n^{TPES}$, mass fraction (%) and degree of polymerization of PBT segments, $\overline{X}_n$, calculated from $^1$H-NMR spectra; interval of melting and degree of crystallinity, $w_c^{DSC}$, determined by DSC*

| Sample | $\overline{M}_n^{PDMS}$ g/mol | mass% PBT (NMR) | $\overline{X}_n$ (PBT) (NMR) | $\overline{M}_n^{TPES}$(NMR) g/mol | Interval of melting (DSC) °C | $w_c^{DSC}$ % |
|---|---|---|---|---|---|---|
| | | | Series I | | | |
| TPES1 | 600 | 59.2 | 3.8 | 15400 | 160–205 | 18.5 |
| TPES2 | 920 | 59.1 | 5.9 | 17700 | 200–225 | 19.1 |
| TPES3 | 1240 | 60.0 | 8.3 | 15200 | 205–225 | 20.1 |
| TPES4 | 2220 | 62.9 | 16.9 | 8300 | 207–227 | 22.6 |
| | | | Series II | | | |
| TPES30 | | 76.2 | 15.4 | 25000 | 200–225 | 23.3 |
| TPES40 | | 69.5 | 11.0 | 34700 | 200–225 | 20.8 |
| TPES45 | 1080 | 58.7 | 6.8 | 35000 | 192–220 | 17.2 |
| TPES50 | | 53.3 | 5.5 | 23700 | 195–220 | 15.0 |
| TPES60 | | 39.2 | 3.1 | 10600 | 190–218 | 11.4 |

It should be noticed that the degree of polymerization of the hard PBT segments was in very similar range in both TPES series.

Dynamic mechanical analysis was performed in order to investigate the influence of the structure and composition of described TPES samples on some rheological parameters. The dependence of the storage, *G'*, and loss, *G''*, shear moduli, tan $\delta$ and complex dynamic viscosity, $\eta*$, on temperature and frequency was followed in these experiments. The rheological measurements were performed under torsion rectangular conditions on molded polymer bars in the temperature range from 30 to about 200 °C, and in the dynamic shear mode between two parallel plates, in the temperature range between 170 and 250 °C. The compositions, molar masses, some DSC data and some rheological parameters of the examined TPESs are given in Table 2.

The recorded changes of the complex dynamic viscosity with temperature and frequency are presented in Figures 3 and 4. From the complex dynamic viscosity measurements, it can be concluded that the synthesized TPES show pseudoplastic behavior over the whole studied temperature range (Figure 3). The values of the Newtonian complex viscosity $\eta*$ at 230 °C, which could be used as an indicator of the molar mass of copolymer, were in the range from 5 to 150 Pa s in Series I and in the range from 10 to 240 Pa s in Series II (Table 2). Increasing the length of PBT segments leads to a decrease in the flexibility of the copolymer chains. Hence, the values of the Newtonian complex viscosity, $\eta*$ (230 °C), increased rapidly, which is particularly pronounced in Series II.

The viscoelastic properties of the TPESs are presented as mechanical spectra by following the dependence of the storage, *G'*, and loss, *G''*, moduli and tan $\delta$ peak on temperature at a fixed frequency of 6.31 rad/s (Figure 5). The spectra show two regions of viscoelastic behavior from 30 to 250 °C – a rubbery plateau region and a flow region. In the rubbery plateau region, the storage and the loss modules decrease slowly with tempe-

*Table 2. Complex dynamic viscosity, $\eta*$, the storage, G', shear modulus, the crossover temperature, $T_{G'=G''}$, and the microphase separation transition temperature, $T_{MST}$, of copolymers*

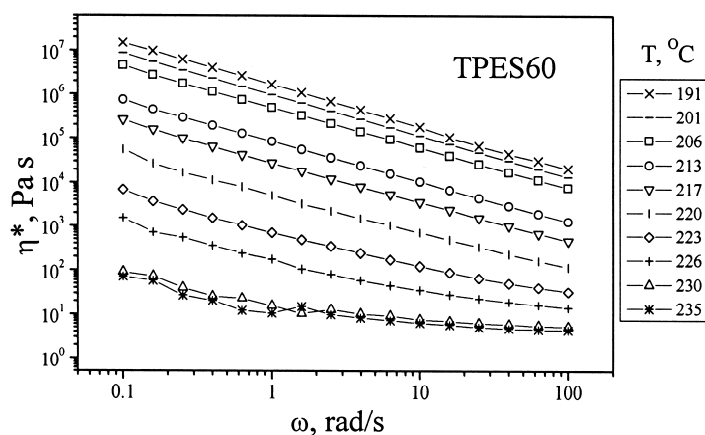| Sample | $\eta*$ / Pa s (at 230 °C) | G' / MPa (at 195 °C, parallel plates) | $T_{G'=G''}$ / °C | $T_{MST}$ / °C |
|---|---|---|---|---|
| | | Series I | | |
| TPES1 | 5 | 0.18 | 212 | 220 |
| TPES2 | 140 | 4.8 | 232 | 234 |
| TPES3 | 150 | 0.14 | 230 | 234 |
| TPES4 | 100 | 0.14 | 234 | 233 |
| | | Series II | | |
| TPES30 | 240 | 0.71 | 231 | 234 |
| TPES40 | 100 | 0.89 | 228 | 233 |
| TPES45 | 70 | 3.6 | 232 | 234 |
| TPES50 | 65 | 0.041 | 228 | 227 |
| TPES60 | 10 | 1.5 | 220 | 230 |

Figure 3. Complex dynamic viscosity, $\eta^*$, versus frequency, at different temperatures for the sample TPES60.
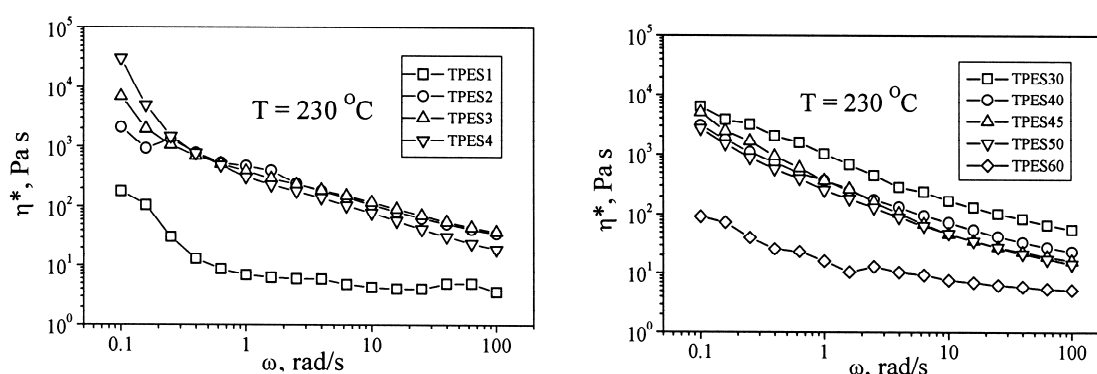


Figure 4. Complex dynamic viscosity, $\eta^*$, of the TPES samples of Series I and II in dependence on the frequency, at 230 °C.

rature due to the incomplete homogeneity of the samples [14]. The rubbery plateau region is characteristic for chemically or physically cross-linked polymers and also for amorphous polymers of high molar masses. The two-phase microstructure of the TPESs, which is a consequence of the chemical incompatibility of physically cross-linked PBT segments and amorphous PDMS segments, is responsible for the appearance of the rubbery plateau region.

The rheological properties of TPESs were investigated in the solid and melt state, therefore the measurements were performed with two different geometries, *i.e.*, rectangular bars and parallel plates (above 170 °C). The change of the sample geometry from the polymer bars in the lower temperature region to the polymer discs in the higher temperature region is marked in the Figure 5. Because of this change, a quite large step is noticeable at some curves – for example, two logarithmic decades for the sample TPES40. The appearance of this large step, when the geometry of the sample is changing, can be attributed to the slippage of the sample due to migration of siloxane segments on the surface of discs, which has been described in the literature [34].

The storage modulus of the TPESs in the rubbery plateau increases with increasing content of hard segments due to the increasing content of crystallizable PBT.

The increase in the storage shear modulus is attributed to an increase in the PBT crystallinity and consequently to an increase in the physical crosslink density, which makes the polymer stiffer in the rubbery plateau. The values of the storage modulus in the rubbery plateau region were in range from 10 to 100 MPa, while the values of the loss modulus were lower, from 1 to 10 MPa. The results show that $G'$ depends on the mass fraction of the hard PBT segments as well as on the degree of the crystallinity ($w_C^{DSC}$, determined by DSC) of TPESs (Figure 6). Thus, the sample TPES30, with 76.2 mass% of PBT and $w_C^{DSC}$ of 23.3% had higher $G'$ values in comparison with the samples TPES40, TPES45 and TPES2, with the degree of crystallinity in the range from 17.2 to 20.8%. The samples TPES2 and TPES45, with 59.1 and 58.7 mass% of PBT segments had very similar $G'$ values in the rubbery plateau region (Table 2).

The transition from the rubbery plateau region to the flow region was investigated on polymer discs, between two parallel plates, in the temperature range from 170 to 250 °C. Change of the $G'$, $G''$ and tan $\delta$ with temperature for the sample TPES45 is presented in Figure 7. Figure 8 presents the changes of $G'$ with temperature for both TPES series, while in Table 2 $G'$ values at 195 °C are given.
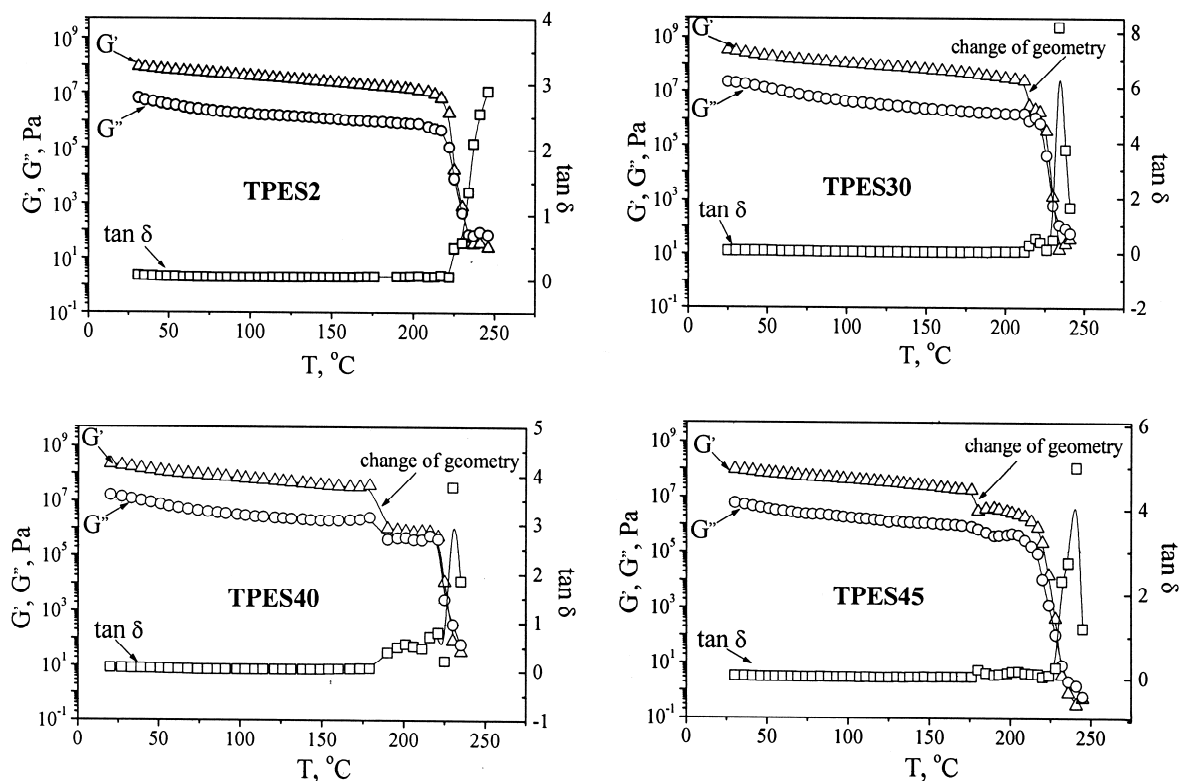
*Figure 5. Storage, G', and loss, G'', shear modulus and tan δ of some of TPES samples in dependence on the temperature, at 6.31 rad/s (torsion rectangular conditions + parallel plates).*
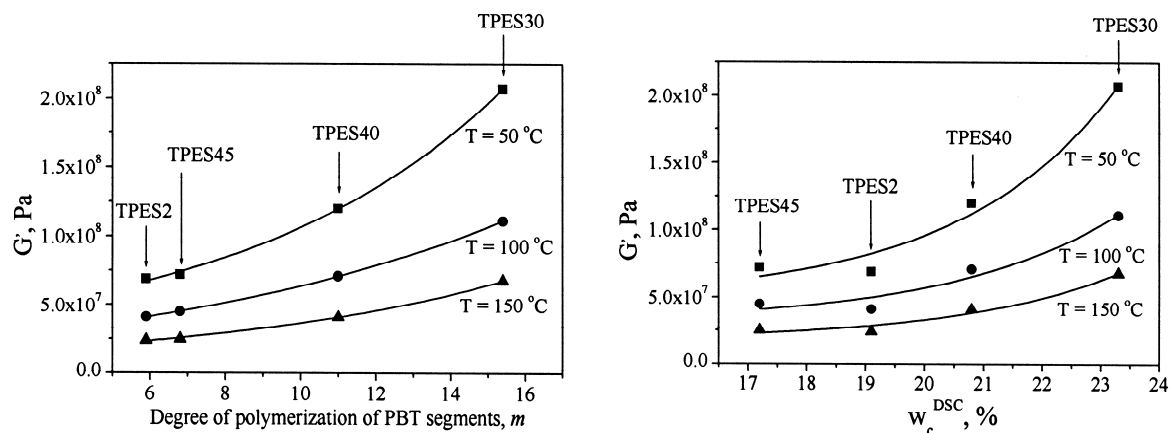


*Figure 6. Storage, G', shear modulus of TPESs in a rubbery plateau region versus: A) degree of polymerization of PBT segments and B) degree of crystallinity at different temperatures (50, 100 and 150 °C).*

Surprisingly, the sample TPES2 in Series I showed significantly higher *G'* value at 195 °C (4.8 MPa), in comparison with *G'* values of all other samples, which were ranged from 0.14 to 0.18 MPa (Table 2). The reason for this phenomenon could be better arrangement of crystallites in the sample TPES2, regardless of the similar degree of crystallinity of TPES2 with other samples of Series I. The storage modules of the sample TPES1 decreased slowly, indicating their slower melting in comparison with the other samples TPES2, TPES3 and TPES4. This is in agreement with DSC results, which show qui-

te broad melting interval for TPES1 while melting intervals for the samples TPES2 to TPES4 became more narrow (Table 1).

In Series II, *G'* values at 195 °C were ranged in very narrow region, between 0.71 and 3.6 MPa, with exception of the sample TPES50, which had *G'* value of 0.041 MPa (Table 2). The reason for significantly lower *G'* value for the sample TPES50 was probably degradation (hydrolysis) of the ester bonds in copolymer, which occurred before dynamic mechanical measurements. The melting of the sample TPES60 was the slowest (*G'*
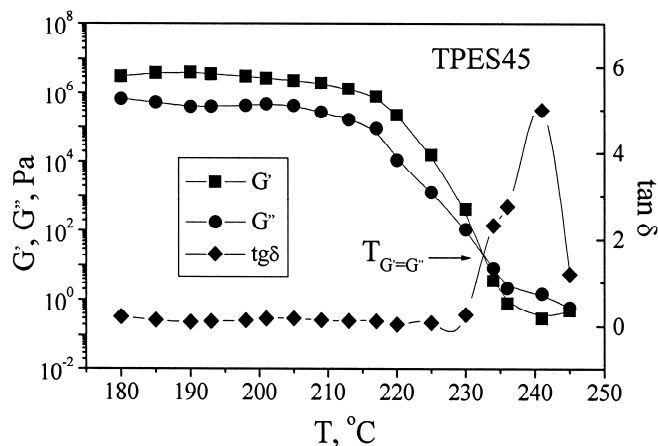
*Figure 7. Storage, G', and loss, G'', shear modulus and tan δ of sample TPES45 in dependence on the temperature, at 6.31 rad/s (parallel plates).*
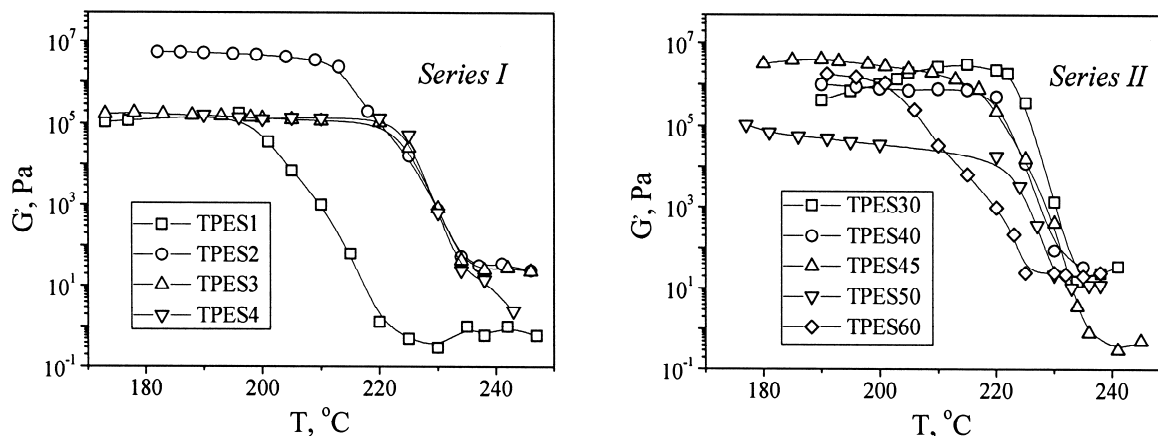


*Figure 8. Storage, G', shear modulus of the samples of series I and II, in dependence on the temperature, at 6.31 rad/s (parallel plates).*

decreased very slowly) which was in agreement with DSC data, showing the largest melting interval for TPES60.

From Figure 7, only a transition from the rubbery plateau region to the flow region can be observed. The crossover temperature, $T_{G'=G''}$, when $G'$ is equal to $G''$ (*i.e.* tan $\delta$ = 1) corresponds to the transition from the rubbery to the flow region. Below the crossover temperature, the behavior of the TPESs is mainly elastic, *i.e.* $G' > G''$, and above this temperature the behavior changes to viscous ($G'' > G'$) [35]. The crossover temperature, which was in range from 212 to 234 °C (Table 2), corresponded very well to the temperature of the end of the melting process determined by DSC. This result shows that the elastic behaviour is dominant as long as crystallites exist in the sample.

An important rheological parameter for phase segregated copolymers, such as TPESs, is the microphase separation transition temperature, $T_{MST}$, (also referred to as the order-disorder transition) [31,36–38]. At room temperature, TPESs consist of a crystalline PBT-phase,

which is dispersed in an amorphous PDMS-phase. However, as the temperature increases above a certain critical value, the size of the PBT-crystallites begins to decrease and the ordered microdomain structure changes to a disordered homogeneous phase (isotropic melt) at $T_{MST}$. The microphase separation transition temperatures for the TPESs can be determined from Figure 9, as temperature at which $G'$ or $G''$ stop to vary and also from Han's diagrams – plots of log $G'$ versus log $G''$ (Figure 10). The Han's diagrams show that microstructure transformation manifests by changes in the shape and slope of curves $G'$ *vs.* $G''$ as the temperature increases. At $T_{MST}$ and above it, log $G'$ versus log $G''$ plots cease to vary with temperature. In other words, $T_{MST}$ is the lowest temperature at which polymer melt is isotropic. The microphase separation transition temperatures for the investigated TPESs were in range from 220 to 234 °C (Table 2) and were about ten degrees higher than the end of the melting process determined by DSC. The $T_{MST}$ values were in general higher for the samples with higher content and length of PBT segments.
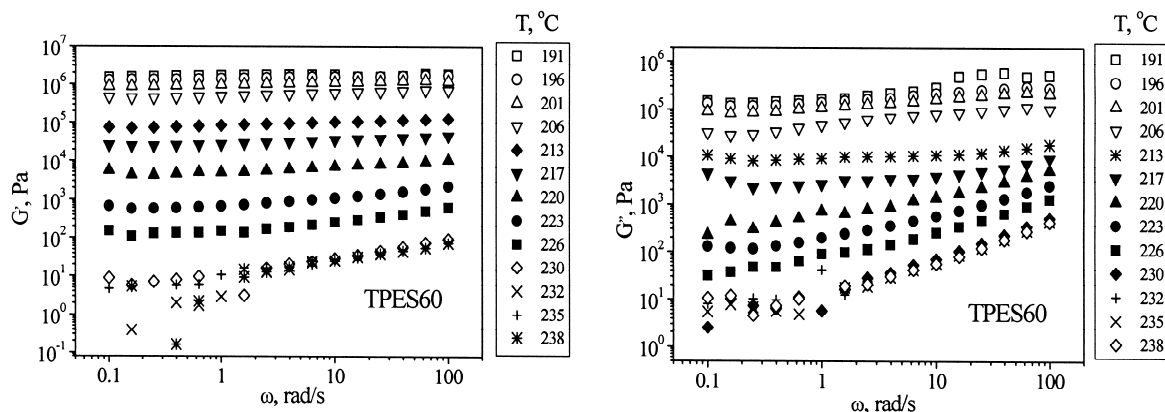
*Figure 9. Storage, G', and loss, G", shear modulus of sample TPES60 in dependence on the frequency, at different temperatures (parallel plates).*
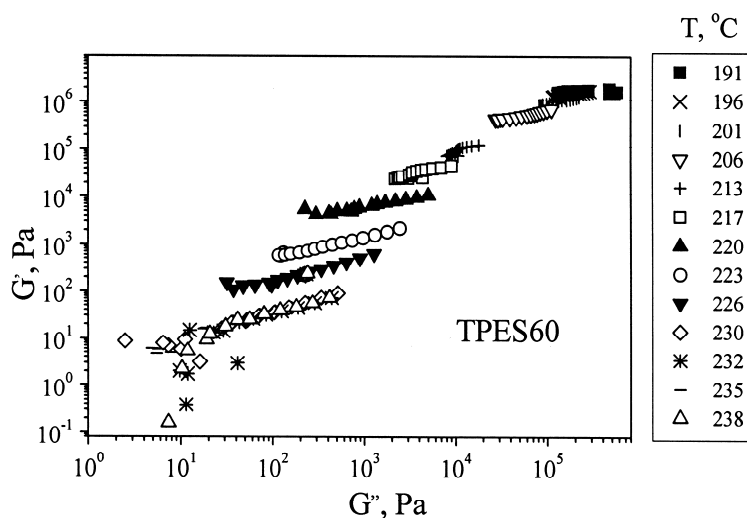


*Figure 10. Log G' versus log G" for the sample TPES60 at different temperatures (Han's diagram).*

## CONCLUSIONS

Two series of thermoplastic poly(ester-siloxane)s, based on hard poly(butylene terephthalate) segments and soft poly(dimethylsiloxane) segments were analyzed by dynamic mechanical spectroscopy in order to investigate the relationship between the structure of copolymers and their rheological properties. In the first series the lengths of both the hard and soft segments were varied while the mass ratio of the hard to soft segments was about 60 mass%. In the second series, the length of the soft PDMS segment was constant, while the mass ratio of hard and soft segments was varied from 60/40 to 40/60. The rheological measurements of TPESs, performed under torsion rectangular conditions, showed that the storage and loss modules decreased slowly with temperature in the rubbery plateau region, due to inhomogeneity of samples. Further, the obtained results also showed that the storage modulus in a rubbery plateau region increased with increasing total degree of crystallinity of the copolymers. The measurements performed in the dynamic shear mode showed that a microphase reorganization occurred during the melting process. The microphase separation transition temperatures, determined from Han's diagrams were in range from 220 to 234 °C. In the isotropic molten state, the dynamic complex viscosity increased with increasing content of PBT segments, as well as with their length.

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## IZVOD

REOLOŠKO PONAŠANJE TERMOPLASTIČNIH POLI(ESTAR-SILOKSANA)

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(Naučni rad)

Dve serije termoplastičnih elastomera (TPES) na bazi poli(dimetilsiloksana) kao mekog segmenta i poli(butilentereftalata) kao tvrdog segmenta su analizirane dinamičko-mehaničkom spektroskopijom. U prvoj TPES seriji varirane su dužine tvrdih i mekih segmenata dok je njihov maseni odnos bio skoro konstantan (oko 60 mas%). U drugoj seriji, odnos tvrdih i mekih segmenata je variran u opsegu od 60/40 do 40/60, dok je dužina mekih PDMS segmenata bila konstantna. Ispitan je uticaj strukture i sastava TPES kopolimera na reološka svojstva, kao što su kompleksni dinamički viskozitet, $\eta^*$, moduli sačuvane, $G'$, i izgubljene energije, $G''$, i temperatura mikrofaznog razdvajanja, $T_{MST}$. Dobijeni rezultati su pokazali da su uzorci sa većim stepenom kristaliničnosti imali i veće module sačuvane energije u gumolikom platou. Reološka merenja su takođe pokazala da svi TPES uzorci ispoljavaju mikrofaznu reorganizaciju u procesu topljenja. Temperature mikrofaznog razdvajanja su bile u opsegu od 220 do 234 °C. U izotropskom rastopu, kompleksni dinamički viskoziteti su rasli sa povećanjem sadržaja i dužine PBT segmenata.

Ključne reči: Poli(estar-siloksani) • Reologija • Kompleksni dinamički viskozitet • Moduli sačuvane i izgubljene energije • Temperatura mikrofaznog razdvajanja
Key words: Poly(ester-siloxane)s • Rheology • Complex dynamic viscosity • Storage and loss shear modulus • Microphase separation transition temperature